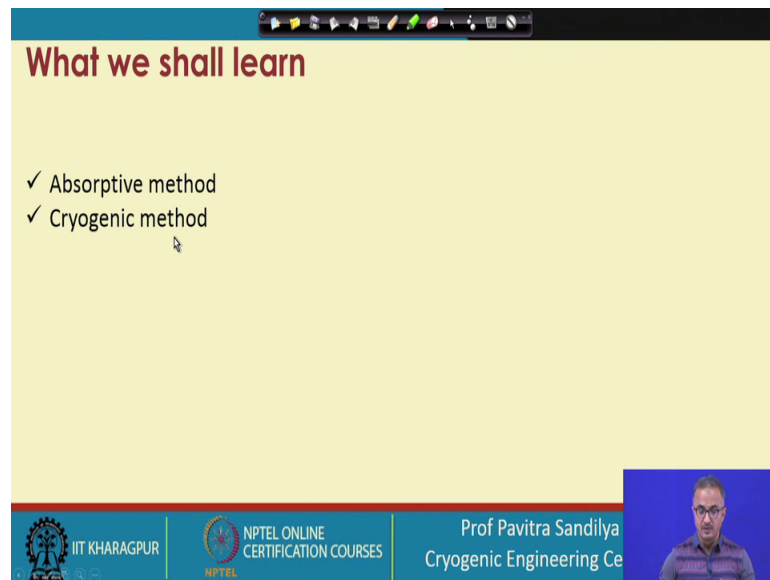


Upstream LNG Technology
Prof. Pavitra Sandilya
Department of Cryogenic Engineering Centre
Indian Institute of Technology, Kharagpur

Lecture – 45
Nitrogen removal in natural gas system- I

Welcome today we shall learn something about the removal of the nitrogen and this nitrogen can be removed in various manners. In this particular lecture, we shall be looking into absorption and the cryogenic distillation processes for the removal of the nitrogen from the natural gas.

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What we shall learn

- ✓ Absorptive method
- ✓ Cryogenic method

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So, what we shall learn? The absorptive method and the cryogenic method for the removal of nitrogen.

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Nitrogen removal

- ✓ Needed to
 - Increase the heating value of natural gas to make pipeline quality gas,
 - Exploit sub-quality natural gas reserve (> 2 mol% carbon dioxide, 4 mol% nitrogen, 4 ppm hydrogen sulfide),
 - Avoid stratification and roll-over during LNG storage and transport,
 - Obtain nitrogen for use in enhanced oil recovery,
 - Obtain “end-flash” gas (mixture of methane and nitrogen) from LNG plant to adjust the heating value of the sales gas,
 - Separate helium from nitrogen in a helium recovery unit.

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First is that why we need to remove nitrogen? The first thing is that it increases the heating value, to increase the heating value of the natural gas to make pipeline quality gas and presence of nitrogen we will reduce the heating value of the natural gas, so we need to remove it. And then if we want to exploit some sub quality natural gas reserve then also we need to remove nitrogen.

And by sub quality we mean that that reserve has more than 2 mole percent of carbon dioxide, more than 4 mole percent of nitrogen and more than 4 ppm of hydrogen sulfide. And we also need to see that whenever we are storing this kind of natural gas there could be possibility of stratification. This comes due to a difference in the densities which is caused by the heat leakage form the ambient, so that the liquid which is near the wall gets heated up and starts moving up and the liquid which is colder on the inner side they will start coming down

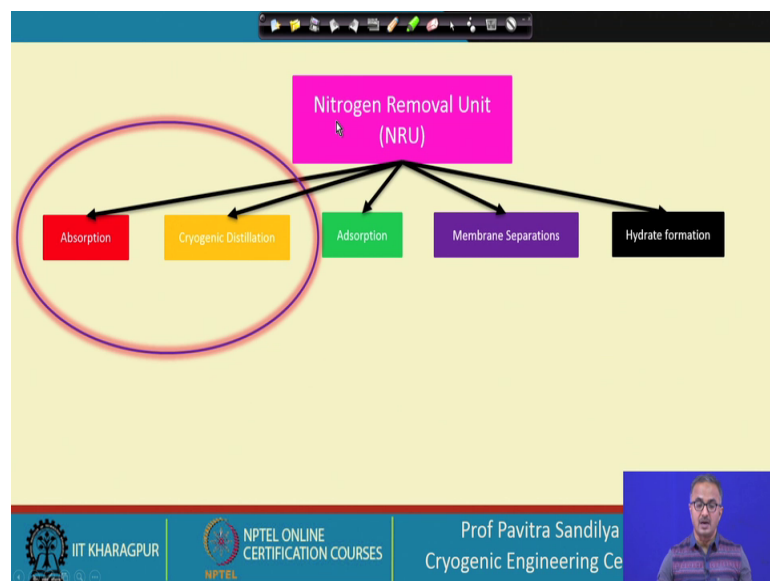
So, this kind of natural, this kind of temperature gradient in the system causes a difference in the densities and this causes some kind of stratification of the temp the, this various density layers and there is a roll over phenomena that occurs that certainly we find that, the upper layer, which is the lighter layer, because it starts losing the lighter components from the surface due to evaporation and the in bottom we have the heavier layer.

And due to the thermal stratification what happens the heavier layer starts tend to move up. And because it cannot move up initially, and with time what happens that the heavier layer in the; at the bottom starts expanding. And suddenly there could be a break down you can say the, due to which the whole mass of the liquid a gets into a some kind of a roll over phenomena; that is the top the liquid comes down and the bottom liquid moves up and this is a roll over phenomena that occurs during the thermal stratification

So, and this happens during the LNG storage; so, for that we need to remove nitrogen, because nitrogen is the lighter component and it can get easily evaporated from the top layer. So, this roll over phenomena can be avoided when we have less amount of nitrogen. And this nitrogen can also be used for enhanced oil recovery, to recover any kind of oil residual oil which remain in the cervices of the sediment in the sub c. So, those residual oil can be recovered using nitrogen.

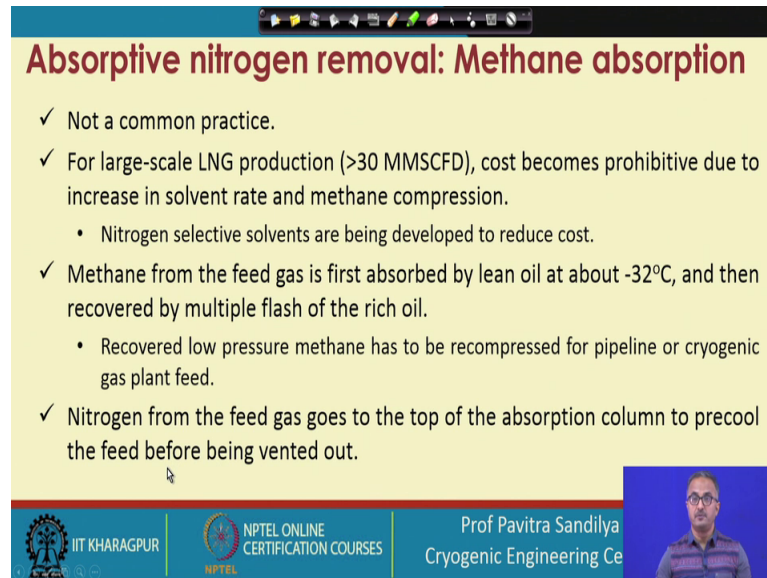
Earlier we also we learn that carbon dioxide can also be used for getting this enhanced oil recovery. And then we have to obtain end flash gas; that means, a mixture of methane and nitrogen from the LNG plant, which are used to adjust the heating value of the sales gas and also we can separate helium from nitrogen in a helium recovery unit, because natural gas is the source of commercial production of the helium and helium is obtain from this NRU unit; that is the nitrogen recovery unit

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So, in the nitrogen removal unit we have several processes absorption, cryogenic distillation, adsorption, membrane separation and hydrate formation. In this lecture we shall be learning about absorption and cryogenic distillation.

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Absorptive nitrogen removal: Methane absorption

- ✓ Not a common practice.
- ✓ For large-scale LNG production (>30 MMSCFD), cost becomes prohibitive due to increase in solvent rate and methane compression.
 - Nitrogen selective solvents are being developed to reduce cost.
- ✓ Methane from the feed gas is first absorbed by lean oil at about -32°C , and then recovered by multiple flash of the rich oil.
 - Recovered low pressure methane has to be recompressed for pipeline or cryogenic gas plant feed.
- ✓ Nitrogen from the feed gas goes to the top of the absorption column to precool the feed before being vented out.

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Now, what is absorption? It is not a very common practice and the cost becomes quite high when we talk of large scale of LNG production; that is a more than 30 millions cubic feed per day, standard cubic per day. Now we become the; for large amount of LNG it becomes quite costly, because we need to have a solve, high solvent rate and we have to also compress the methane, so this increases the cost.

And if we can develop some kind of solvent which are nitrogen selective, then perhaps we can reduce the cost. Then we do not have to compress methane which is in larger amount, we can just compress nitrogen which is in smaller amount. So, only the cost will be reduced because it is based on the nitrogen separation; rather than methane separation.

In this process, the methane gas is first absorbed by some oil at very low temperature and then recovered by multiple flash of the rich oil, and the recovered low pressure methane has to be recompressed for pipeline or cryogenic gas plant feed. That is why researchers are working on to selectively remove nitrogen rather than methane, so that we can also avoid this subsequent flash operations of the methane rich oil. So, nitrogen from the feed gas goes to the top of the absorption column to pre-cool the feed before being vented out.

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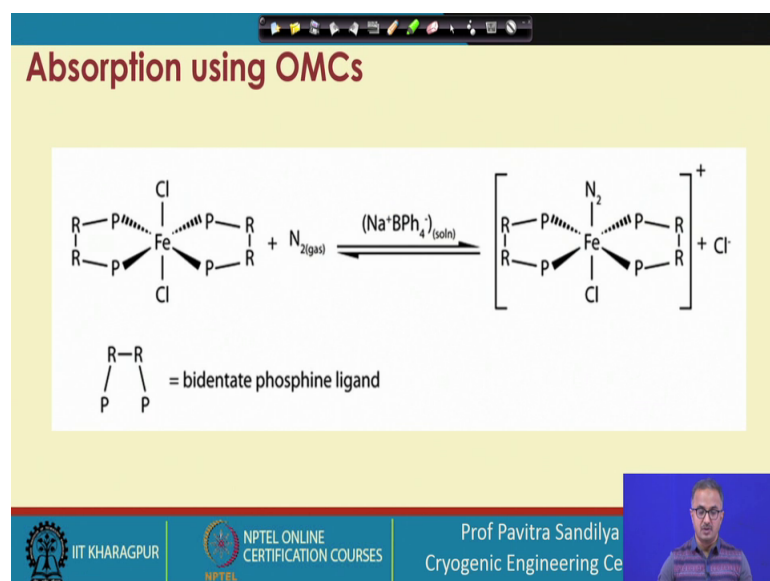
Absorptive nitrogen removal: Nitrogen absorption

- ✓ Organo-metallic complexes (OMCs) have been developed to absorb nitrogen.
- ✓ Potentially competitive to cryogenic NRU
- ✓ Main barriers:
 - High cost of OMC,
 - Contamination of OMC by water and hydrogen sulfide
 - OMC is pyrophoric (ignite spontaneously if brought in contact with air): Causes safety and material handling problems.

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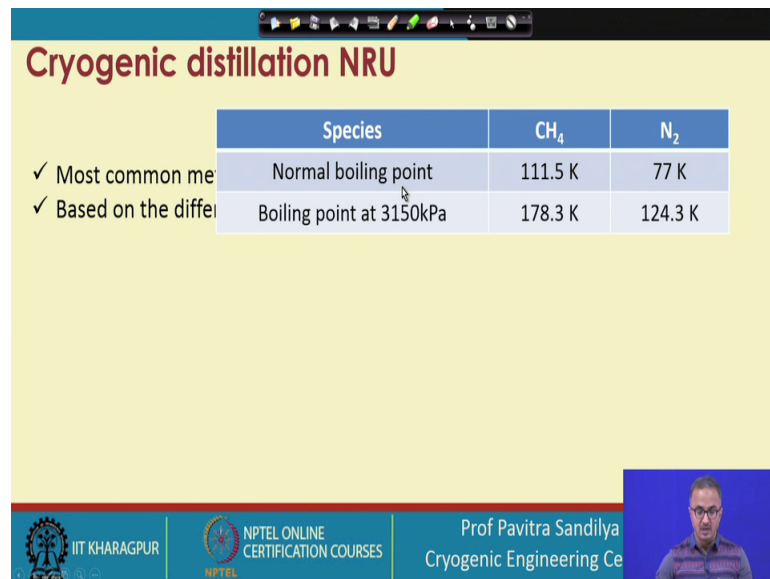
Now here we have some organo metallic complexes to absorb nitrogens, they are still developmental stage. And if they can be developed properly; we will find that they can be potentially competitive to cryogenic nitrogen removal units. And the several barriers challenges are there in the development of this OMCs that there the, their cost is high and these organo-metallic complexes get contaminated in the presence of water and H₂ S and their pyrophoric, means they can catch fire in contact with air spontaneously and this causes safety and other material handling problems.

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So, here is the typical OMC which is shown that how it absorbs the nitrogen

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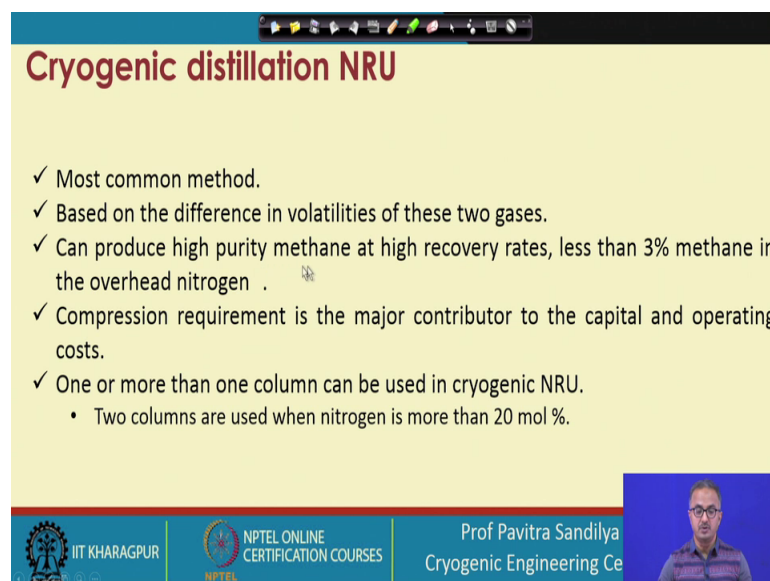
Cryogenic distillation NRU

	Species	CH ₄	N ₂
✓ Most common me	Normal boiling point	111.5 K	77 K
✓ Based on the diffe	Boiling point at 3150kPa	178.3 K	124.3 K

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Now, next we have the cryogenic distillation to remove nitrogen, and this is the most common method, it is based on the difference in the volatilities of the two gases that is methane. And here we find how the boiling points of methane and nitrogen differ at two different pressure. Normal boiling point means it is at one atmosphere.

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Cryogenic distillation NRU

- ✓ Most common method.
- ✓ Based on the difference in volatilities of these two gases.
- ✓ Can produce high purity methane at high recovery rates, less than 3% methane in the overhead nitrogen .
- ✓ Compression requirement is the major contributor to the capital and operating costs.
- ✓ One or more than one column can be used in cryogenic NRU.
 - Two columns are used when nitrogen is more than 20 mol %.

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Then distillation can produce high purity of methane at high recovery rates and less than 3 percent methane in the overhead nitrogen; that means, we are also losing less amount

of methane with the overhead nitrogen, and compression requirement is the major contributor to the capital and operating cost. We have to compress the gas before it can be sent for distillation and one or more than one column may be used in the cryogenic nitrogen removal unit. Two columns are used when the amount of nitrogen is more than 20 mole percent.

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Single column cryogenic distillation NRU

- ✓ Freezable contaminants (H_2O , CO_2) and higher hydrocarbons are removed from NG.
- ✓ NG is cooled, throttled and fed to an intermediate stage of the distillation column at pressures 1300 – 2800 kPa.
- ✓ Rejected N_2 -rich vapor drawn from the top has less than 1 mol% CH_4 .
- ✓ Methane-rich (about 98 mol% CH_4) stream is drawn from the bottom.
- ✓ The bottom product can be reheated with the feed gas.

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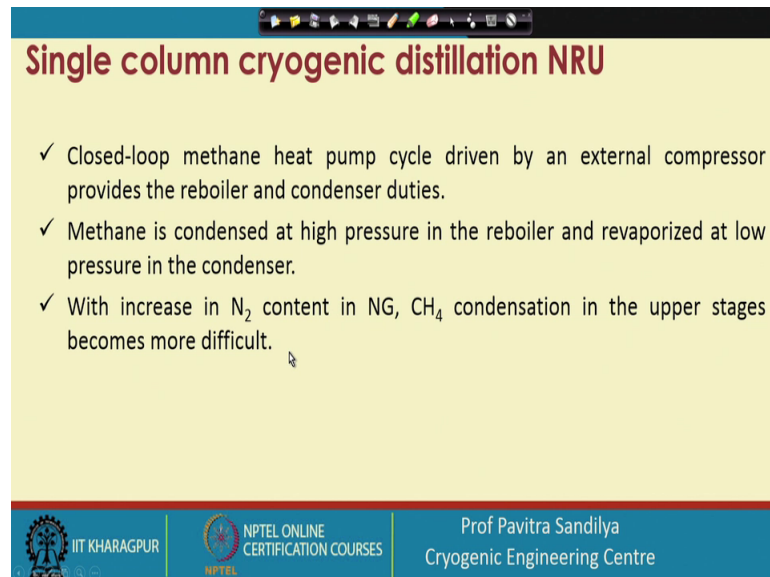
So, here first we go with a single column cryogenic distillation, it is this particular column. Now what we do? This is the natural gas with a at about this 3000 kilo Pascal which is going to the column. And this column, first we remove the water, the carbon dioxide and hydrocarbons, because they can get frozen inside the pipelines.

So, before it is, this nitrogen gas is said to the distillation column at very low temperature we remove H_2O , CO_2 and other higher hydrocarbons. Then what happens? This N_2 , this natural gas is cooled and it is cooled by the out coming nitrogen, cooled nitrogen and also the bottom liquid which is coming from the actual column. So, this liquids are also helping to cool the feed natural gas and again it is taken to a expansion valve; that is called the Joule Thomson valve, and through which ideally and isenthalpic expansion; that is constant enthalpy expansion goes. And because of this expansion this is natural gas gets further cooled, and it forms two phases which is required for the distillation.

And then it goes into the column at a pressure drop about 1300 to 2800 kilo Pascal and this is because nitrogen is lighter than methane, so we find that it goes of the column and

methane will be coming down the column. So, this nitrogen has less than 1 mole percent of methane in it. And the methane rich liquid that is about 98 mole percent of methane is coming, taken from the bottom and it, as I said it helps to cool down the incoming nitrogen and before it is taken for compression and the up gradation of the natural gas.

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Single column cryogenic distillation NRU

- ✓ Closed-loop methane heat pump cycle driven by an external compressor provides the reboiler and condenser duties.
- ✓ Methane is condensed at high pressure in the reboiler and revaporized at low pressure in the condenser.
- ✓ With increase in N_2 content in NG, CH_4 condensation in the upper stages becomes more difficult.

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Now, we are using this heat pump here. This heat pump is used may, using methane as the working gas and this heat pump is used go to cool down; the nitrogen at the top and the heat up the, for the reboil reboiler heat duty for the distillation.


So, both condenser reboiler duties are given by this particular heat pump, and methane is condensed at high pressure in the reboiler and revaporized at the low pressure in the condenser. Whereas, with increasing the nitrogen content in natural gas, methane condensation in the upper stages becomes more and more difficult.

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Single column cryogenic distillation NRU

- ✓ Operating flexibility of single-column NRU is limited to maximum N_2 -concentration in feed gas to 20 mol %, because:
 - I. Critical pressures of methane-nitrogen mixtures, which limits the maximum pressure in the distillation column to about 2800 kPa, and
 - II. Maximum practical temperature of methane after throttling valve of heat-pump cycle.

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Now, there is a operating flexibility of the single column is limited when the nitrogen is less than about 20 mole percent, because critical pressures of methane nitrogen mixtures which limits the maximum pressure. Because of beyond the critical pressure we cannot condense, we have to always keep within the critical pressure so get it at the two phases.

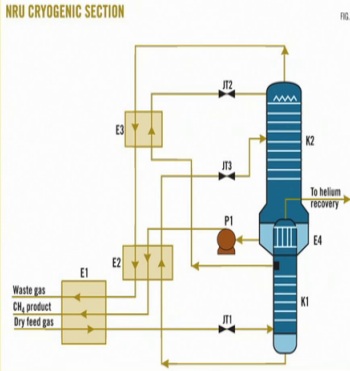
So, that this this is the, this critical pressure limits this methane nitrogen mixture two about; that means, we cannot go beyond this particular pressure about 2800 kilo Pascal, and maximum practical temperature of the methane after throttling is also the limitation.

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Double column cryogenic distillation NRU

- Raw NG is decontaminated from H_2O , CO_2 and higher hydrocarbons and fed to the high pressure (HP) lower column (K1) at 1000 – 2500 kPa.
- Some nitrogen is removed due to flash. The liquid from bottom of K1 column is subcooled in E2 and fed to the low pressure (LP) upper column (K2) at 150 kPa.

NRU CRYOGENIC SECTION



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Now, for higher amount of the nitrogen we use the double column cryogenic distillation. In this what we find? That we the wrong product; that is this particular wrong drive feed gas is the; from; again from this we are removing the H₂O carbon dioxide and hydro hydrocarbons is fed to the lower column.

So, here we have two columns; one is the lower column another is upper column. Lower column act operates at higher pressure, whereas, this top column act operates at a lower pressure. So, first we feed this take, which is taken to the lower column and as we know that in this double column are used, when we need both P order heavier component and the lighter component in the single. In the single single column we were getting the only the P order means lighter component.

So, here we are using we need both nitrogen and methane we can get. So, this is row feed which is taken to the lower column that is at high pressure column to at about 1000 to 2500 kilopascal, and some nitrogen is removed due flash. And the liquid from the bottom of this column, this column is taken as the feed after this throttling, it is taken as a feed for the top column, upper column and which operates at about 150 kilo Pascal.

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Double column cryogenic distillation NRU

- CH₄-rich bottom product and N₂-rich top product of K2 column is pumped through crude subcooler E2, to cool the bottom liquid from K1 column which enters K2 column via a JT valve J3 (and flashes).
- K2 column carries out the main distillation to separate CH₄ and N₂.
- Reboil to K2 column is provided by condensing nitrogen at high pressure in the top of the lower column.

NRU CRYOGENIC SECTION

FIG. 2

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And then we find that this methane rich bottom product of and this nitro; from these particular column this thing is the methane rich and this is the nitrogen rich, and these two streams are taken here before they are taken out, they are passed through this heat

exchanger, three channel heat exchanger to cool down this bottom stream from the bottom column.

So, here we are doing some kind of heat integration to internally cool down the hot stream. And then this is the nitrogen is not to be used it is waste gas and we are getting the product methane from the bottom of the top column.

And then in this particular column is responsible for the separation of the methane and the nitrogen. And again this whatever reboiler duty we need at the bottom of this column is provided by the condensation of the nitrogen from the bottom column at the higher pressure

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Double column cryogenic distillation NRU

- N₂-rich vapor from HP column is condensed to provide reflux for LP column.
- LP column produces high purity N₂ which is used to cool the N₂ reflux fed to the LP condenser, subcool bottoms of the HP column and precool the feed gas.
- For LNG production, methane rich bottom products from LP column may remain liquid.

NRU CRYOGENIC SECTION

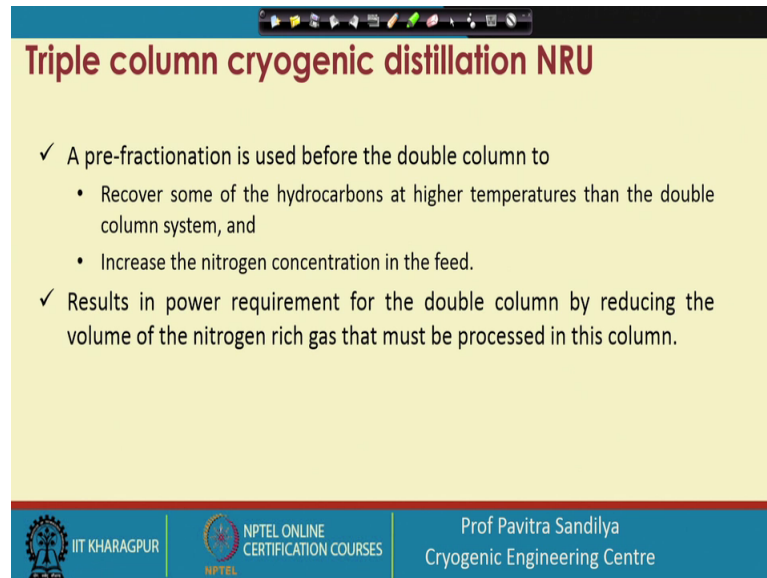
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And here we find the nitrogen rich vapor from the high pressure column is condensed to provide the reboiler duty for the, reboiling this liquid in the top column, and the low pressure column produces high purity nitrogen which is used to cool the nitrogen reflux, fed to the low pressure condenser, sub cool bottoms of the high pressure column and the pre cool the feed gas

So, this particular. From low pressure column this nitrogen is used in this particular heat exchanger, in this heat exchanger and in this heat exchanger. So, we are able to; this is a reflux and this is the feed cooling, and this is the cooling of the this bottom product from the bottom column. So, here all we are using this nitrogen. And for the LNG production,

methane rich bottom products from the low pressure column may remain liquid. So, from here we are getting the methane product which can remain in the liquid phase

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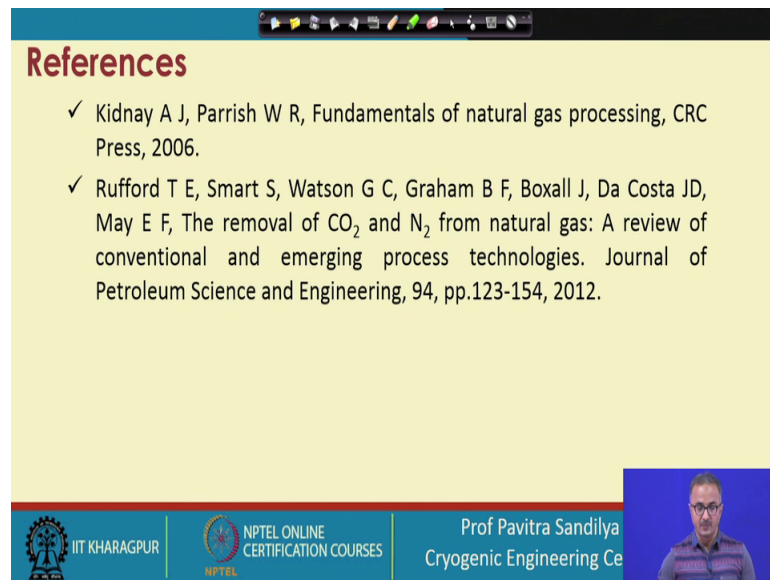
Triple column cryogenic distillation NRU

- ✓ A pre-fractionation is used before the double column to
 - Recover some of the hydrocarbons at higher temperatures than the double column system, and
 - Increase the nitrogen concentration in the feed.
- ✓ Results in power requirement for the double column by reducing the volume of the nitrogen rich gas that must be processed in this column.

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And then we have, we may have a triple column cryogenic distillation in. This is in addition to recover some of the hydrocarbons at higher temperatures than the double column system, and this will be able to increase the nitrogen concentration in the feed. So, we use a separate pre fractionation column before it is send to the double column, and this results in power requirement for the double column by reduces power requirement, by reducing the volume of the nitrogen rich gas that must be processed in the column. So, that is why we are using the three columns for this removal of the nitrogen by distillation.


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So, these are the references which give more detail about the nitrogen's removal.

Thank you.